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(54) SI SUBSTRATE AND ITS SURFACE TREATMENT METHOD

(57)Abstract:

PURPOSE: To provide a Si substrate, which has a stable Si surface structure in a film-making temperature region in epitaxial growth of an oxide, accomplishing connecting to an oxide film which grows crystal structure information, having reproducibility and excellent capacity for mass production, and its surface treatment method.

CONSTITUTION: A Si substrate comprises a Si single crystal, its surface having a 1×1 surface structure formed of alkaline earth, rare earth (including Sc and Y), at least one kind of metal from Zr and Hf, and oxygen.

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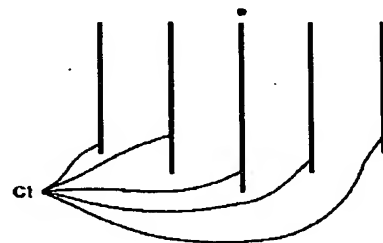
(54) 【発明の名称】 S i 基板およびその表面処理方法

(57) 【要約】

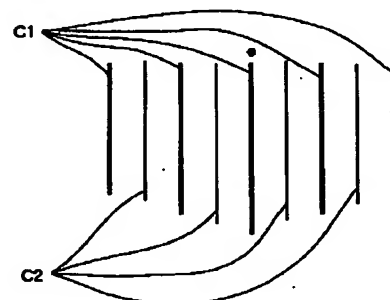
【目的】 酸化物のエピタキシャル成長に際し、成膜温度領域で、S i 表面の構造が安定で、かつ結晶構造情報を成長させる酸化物膜へ伝える役割を果たし、再現性があり、量産性に優れたS i 基板およびその表面処理方法を提供することを目的とするものである。

【構成】 S i 単結晶で構成され、その基板表面が、アルカリ土類、希土類 (S c、Yを含む)、Z r、H f の少なくとも1種類の金属と酸素とにより形成された1×1の表面構造を有する。

(a)



(b)



【特許請求の範囲】

【請求項1】 Si単結晶で構成され、その基板表面が、アルカリ土類、希土類（Sc、Yを含む）、ZrおよびHfの少なくとも1種類の金属と酸素とにより形成された1×1の表面構造を有するSi基板。

【請求項2】 Si単結晶基板表面にSi酸化物層を形成し、その後、真空中で加熱しつつ、アルカリ土類金属、希土類（Sc、Yを含む）、ZrおよびHfの少なくとも1種類の金属と酸化性ガスを表面に供給し、基板表面を、アルカリ土類、希土類（Sc、Yを含む）、ZrおよびHfの少なくとも1種類の金属と酸素とにより形成された1×1の表面構造とすることを特徴とするSi基板の表面処理方法。

【請求項3】 前記Si酸化物層を形成する際、酸化性ガスを導入した真空槽内で、Si単結晶基板を300～700℃に加熱し、真空槽内の少なくとも基板近傍の雰囲気酸素分圧を 1×10^{-4} Torr以上として、0.2～10nmのSi酸化物層を形成する請求項2のSi基板の表面処理方法。

【請求項4】 前記金属の供給を、目的とする金属の蒸発により行い、この蒸発の際、Si単結晶基板の基板温度を600℃～1200℃に設定し、この状態で、酸化性ガスを導入し、真空槽内の少なくともSi単結晶基板近傍の雰囲気酸素分圧を 1×10^{-4} ～ 1×10^{-1} Torrとする請求項2または3のSi基板表面処理方法。

【請求項5】 前記Si単結晶基板を、その（100）面が基板表面となるように用いる請求項2～4のいずれかのSi基板表面処理方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、Si基板およびその表面処理方法に関するもので、基板の表面層の構造に敏感なプロセス、特に、Si基板上への高誘電率薄膜、強誘電体薄膜、超電導薄膜などの酸化物薄膜のエピタキシャル成長用の基板およびエピタキシャル成長プロセス前の基板前処理に使用される表面処理方法に関するものである。

【0002】

【従来の技術】半導体デバイス、たとえば、DRAMにおいて用いられているSiFETにおけるゲートは、酸化膜として通常多結晶またはアモルファスSiO₂膜が使用されMOS構造を構成している。集積化が進むに伴い、MOSキャパシタの寸法は、より小さいものが要求され、現在の集積度では限界にきている。SiO₂の誘電率は約3であり、FETのゲートを働かせるための電荷をMOSキャパシタで確保するには、さらに大きな誘電率を有する誘電体をSiO₂の替わりに用い、かつ良好なMOS特性を得なければならない。SiO₂はSiと非常に相性がよいため多結晶またはアモルファスの状態でSiデバイスに用いられてきた。しかしながら、S

iO₂代替の他材料では、多結晶またはアモルファスの状態では、最適なデバイス特性およびその再現性を確保することは難しい。多結晶中の粒界による物理量の攪乱、アモルファス状態での材料物性値の不安定性が主な原因と考えられており、SiO₂代替の他材料は、Siデバイスに、実際に、用いられていないのが現状である。

【0003】そのため、SiO₂に代わり、単結晶で、誘電率が大きく、MOS（MIS）特性の優れた誘電体薄膜材料が必要とされている。この誘電体薄膜の開発により、集積度のさらに高いLSI、SOI技術による誘電体分離ICなどSOIデバイスの実現が可能となる。

【0004】また、半導体結晶基板であるSi基板上に、強誘電体膜、または超電導膜を形成、集積化した電子デバイスが考案されている。半導体と超電導体または強誘電体を組み合わせることにより、たとえば、半導体と超電導体の組み合わせでは、SQUID、ジョセフソン素子、超電導トランジスタ、電磁波センサーおよび超電導配線LSIなど、半導体と強誘電体では、不揮発性メモリ、赤外線センサー、光変調器および光スイッチOEIC（光・電子集積回路：opto-electronic integrated circuits）などが試作されている。

【0005】これら超電導体材料または強誘電体材料を用いた半導体デバイスにおいて、最適なデバイス特性およびその再現性を確保するためには、超電導体材料および誘電体材料として単結晶を用いることが必要である。多結晶では粒界による物理量の攪乱のため、良好なデバイス特性を得ることが難しい。このことは薄膜材料についても同様で、できるだけ完全な単結晶に近い超電導または誘電体エピタキシャル膜が望まれる。

【0006】近年、誘電体酸化物材料のYSZ（ZrO₂にYをドープさせ安定化させた材料）がSi単結晶上にエピタキシャル成長できることが報告された。YSZは、高い化学安定性、広いバンドギャップ（約5eV）、大きい誘電率（約20）を具備しているためMISキャパシタ、集積度のさらに高いLSI、SOIデバイスに適している。製造については、種々の方法および組成が検討されてきた。例えば、Appl. Phys. Lett., Vol. 53, No. 16, p. 1506-08（1988）には、YSZ酸化物ターゲットを用い、イオンビームスパッタ法により、Si（100）基板上にYSZのエピタキシャル膜が得られることが述べられている。また、上記Japanese Journal of Applied Physics, Vol. 27, No. 8, L1404-05（1988）には、酸素を導入した真空槽内でYSZペレットを電子線銃により蒸発させる蒸着法より、Si（100）基板上にYSZのエピタキシャル膜が得られることが述べられている。更に、Appl. Phys. Lett., Vol. 57, No. 11, p. 1137-39（1990）に

は、YSZターゲットを用いたレーザーアブレーション法により、Si(100)基板上にYSZのエピタキシャル膜が得られることが述べられている。更にまた、Thin Solid Films, 299, 17-23(1993)には、金属Zr上にY片をのせたターゲットを用いた反応性マグネトロンスパッタリング法により、Si(100)基板上にYSZのエピタキシャル膜が得られることが述べられている。

【0007】また、酸化物超電導体および強誘電体についても、Si基板上に結晶成長させる方法が検討されている。応用的に価値のある、おもな酸化物超電導体および強誘電体の結晶構造は、ペロブスカイト構造をとっている。ペロブスカイト型酸化物のエピタキシャル成長は基板の材料と結晶方位に大きく依存し、ペロブスカイト型酸化物をSi基板上へ直接エピタキシャル成長させることは、現在のところ不可能である。そこで、Siにエピタキシャル成長したバッファ層を設け、その上にペロブスカイト型酸化物のエピタキシャル成長させることが、Appl. Phys. Lett., Vol. 54, No. 8, p. 754-p. 756(1989)、Japanese Journal of Applied Physics, Vol. 29, No. 9, L955-57(1990)、特開平2-82585号公報に述べられている。

【0008】このような、誘電体、超伝導体、および強誘電体の酸化物エピタキシャル膜は、Si基板上に結晶成長され、電極形成、微細加工、などの半導体プロセスにより加工される。半導体素子と酸化物エピタキシャル膜を組み合わせることにより、集積度のさらに高いLSI、SOI技術による誘電体分離ICなどSOIデバイス、SQUID、ジョセフソン素子、超電導トランジスタ、電磁波センサーおよび超電導配線LSI、不揮発性メモリー、赤外線センサー、光変調器および光スイッチOEICなどを製造することができる。酸化物のエピタキシャル膜は、粒界などの物理量の攪乱がないため、それぞれの応用で良好な機能を発揮する。

【0009】Si単結晶の表面には、空気中で、SiO₂の自然酸化膜が形成されている。この自然酸化膜が存在すると、Si基板の結晶情報が膜に伝わらず、エピタキシャル成長が不可能になる。

【0010】そこで、上述の方法では、まず、はじめに、Siの清浄面を得るための処理が行われている。

【0011】方法としては、基板を回転しながらエッチングを行う。窒素雰囲気中で、基板を回転させ、高純度アルコールでリンスする。その後、すべて高純度のHF、エタノール、純水(1:10:1)の溶液を滴下しエッチングする。この基板を窒素雰囲気のグローブボックスにいれ移送し、すばやく成膜装置に装着する。さらに、真空槽を 1×10^{-6} Torr以上の高真空に排気し加熱し、成膜する温度にする。この工程で基板表面の汚染を防ぐため、真空槽内はできるだけ清浄に保つようにして

いる。上述の例では、このように注意をはらったSi基板がエピタキシャル成長に用いられその工程は非常に複雑である。また他の方法としては、膜の成長初期にSiの結晶情報を引き出すため、界面制御層を挿入する方法が、Japanese Journal of Applied Physics, Vol. 30, L1415~1417(1991)に示されている。この方法においても、処理条件がに敏感でかつ複雑であり、最適な処理でのみ、酸化物のエピタキシャル成長が実現されるのであって、再現性に乏しい。

【0012】また、一般に、酸化物のエピタキシャル成長は、700℃以上の高温が必要である。上記のように清浄化されたSi表面は、反応性に富み、上記の700℃以上の温度で、真空中においても、残留ガス特に炭化水素と反応を起こし、表面にSiCが形成されることにより基板表面が汚染され、基板表面の結晶が乱れる。乱れたSi基板表面では、結晶情報が膜に十分伝わらず、エピタキシャル成長が不可能になる。

【0013】

【発明が解決しようとする課題】そこで、本発明は、酸化物のエピタキシャル成長に際し、成膜温度領域で、Si表面の構造が安定で、かつ結晶構造情報を成長させる酸化物膜へ伝える役割を果たし、再現性があり、量産性に優れるSi基板およびその表面処理方法を提供することを目的とするものである。

【0014】

【課題を解決するための手段】このような目的は、下記(1)～(5)の本発明により達成される。

(1) Si単結晶で構成され、その基板表面が、アルカリ土類、希土類(Sc、Yを含む)、ZrおよびHfの少なくとも1種類の金属と酸素とにより形成された 1×1 の表面構造を有するSi基板。

(2) Si単結晶基板表面にSi酸化物層を形成し、この後、真空中で加熱しつつ、アルカリ土類金属、希土類(Sc、Yを含む)、ZrおよびHfの少なくとも1種類の金属と酸化性ガスとを表面に供給し、基板表面を、アルカリ土類、希土類(Sc、Yを含む)、ZrおよびHfの少なくとも1種類の金属と酸素とにより形成された 1×1 の表面構造とすることを特徴とするSi基板の表面処理方法。

(3) 前記Si酸化物層を形成する際、酸化性ガスを導入した真空槽内で、Si単結晶基板を300～700℃に加熱し、真空槽内の少なくとも基板近傍の雰囲気酸素分圧を 1×10^{-4} Torr以上として、0.2～10nmのSi酸化物層を形成する上記(2)のSi基板の表面処理方法。

(4) 前記金属の供給を、目的とする金属の蒸発により行い、この蒸発の際、Si単結晶基板の基板温度を600℃～1200℃に設定し、この状態で、酸化性ガスを導入し、真空槽内の少なくともSi単結晶基板近傍の雰

囲気を $1 \times 10^{-4} \sim 1 \times 10^{-1}$ Torrとする上記(2)または(3)のSi基板表面処理方法。

(5) 前記Si単結晶基板を、その(100)面が基板表面となるように用いる上記(2)～(4)のいずれかのSi基板表面処理方法。

【0015】

【発明の作用・効果】本発明によるSi基板は、Si表面が反応性に富み不安定であることに鑑み、Siの結晶表面を露出させずに、基板表面がアルカリ土類、希土類(Sc、Yを含む)、Zr、Hfの少なくとも1種類の金属と酸素により形成された 1×1 の表面構造を有している。この表面は、平坦で周期性が良い結晶表面が現れ、しかも酸化物のエピタキシャル成長に際し、成膜温度領域で、構造が安定であるため、成長させる酸化物膜へ結晶構造情報を良好に伝える。この基板を用いることにより、この基板上に結晶性、表面性の優れた酸化物エピタキシャル膜を再現性よく製造することが可能になる。特に、酸化物エピタキシャル膜結晶において、バルク結晶構造を切断したときに考えられる基板の表面構造は 1×1 構造となるので、この点からも良好なエピタキシャル成長を行わさせることが可能となると考えられる。

【0016】

【具体的構成】本発明のSi基板は、Si単結晶で構成され、その基板表面が、アルカリ土類、希土類(Sc、Yを含む)、Zr、Hfの少なくとも1種類の金属と酸素とにより形成された実質的に 1×1 の表面構造を有する。

【0017】表面構造は、反射高速電子線回折(Reflection High Energy Electron Diffraction: 以下、RHEEDと称する)による像のパターンで調べることができる。例えば、本発明が目的とする 1×1 の表面構造の場合、電子線入射方向が $[110]$ で図1の(a)に示したような1倍周期C1の完全なストリークパターンとなり、入射方向を $[1-10]$ にしても全く同じパターンとなる。一方、Si単結晶清浄表面は、 1×2 、 2×1 、または、 1×2 と 2×1 が混在している表面構造となる。このような場合には、RHEED像のパターンは、電子線の入射方向 $[110]$ または $[1-10]$ のいずれか、または両方で図1の(b)に示したような、1倍周期C1と2倍周期C2を持つパターンになる。本発明の 1×1 の表面構造においては、上記RHEEDのパターンでみて、入射方向が $[110]$ および $[1-10]$ 両方で、図1の(b)の2倍周期C2が見られない。なお、RHEEDから表面1～数原子程度の厚さの情報が得られる。

【0018】またSi清浄表面は、 1×1 構造を示す場合がある。われわれの実験でも何度か観察されたが、 1×1 を示す条件は、不明確で安定に再現性よく 1×1 をSi清浄面で得ることは、現状では不可能である。

【0019】 1×2 、 2×1 、 1×1 いずれの構造のSi清浄面は、真空中、高温で汚染されやすく、特に残留ガス中に含まれる炭化水素と反応し表面にSiCを形成し、基板表面の結晶が乱れる。したがって、Si基板上に酸化膜を結晶成長させる際に適した 1×1 構造を安定に形成することがこれまで不可能であった。

【0020】本発明の 1×1 の表面構造を示す表面は、上記アルカリ土類、希土類(Sc、Yを含む)、Zr、Hfの少なくとも1種類の金属をM、酸素およびSiの相互作用により形成されている。この表面は高温、真空中で汚染されることなく、安定で、酸化物を結晶成長させる基板として最適である。

【0021】金属Mとして、上記の中から2種以上用いるときの量比は任意である。

【0022】なお、上記アルカリ土類金属とは、カルシウムCa、ストロンチウムSr、バリウムBa、ラジウムRa、ベリリウムBe、マグネシウムMgを示す。また、希土類金属とは、イットリウムY、ランタンLa、セリウムCe、プラセオジウムPr、ネオジウムNd、プロメチウムPm、サマリウムSm、ユーロビウムEu、ガドリニウムGd、テルビウムTb、ジスプロシウムDy、ホルミウムHo、エルビウムEr、ツリウムTm、イッテルビウムYb、ルテチウムLuおよびスカンジウムScを示す。

【0023】本発明のSi基板は、その基板表面に、組成 $Zr_{1-x}R_xO_{2-\delta}$ (ここで、RはYを含む希土類金属であり、 $x=0 \sim 0.75$ 好ましくは $0.2 \sim 0.5$ である。また、 δ は通常 $0 \sim 0.5$ である。)およびペロブスカイト等のエピタキシャル膜を良好に生長させることができる。

【0024】上記ペロブスカイト構造を有するエピタキシャル膜とは、具体的には、Bi系酸化物超電導膜、 $YBa_2Cu_3O_{7-8}$ (YBCO)超電導膜等の高温超電導膜、 $BaTiO_3$ 、 $PbTiO_3$ 、PZT、PLZT、その他のPb系ペロブスカイト、その他Bi系ペロブスカイト、Bi層状化合物等の強誘電体膜、さらには、 $La_{1-x}Sr_xCoO_3$ 、 $La_{1-x}Sr_xCa_xRuO_3$ 等の酸化物導電膜が挙げられる。また、 In_2O_3 (Snドープ)、その他酸化物導電膜、Pt、Si、Ge、GaAs等の半導体や金属の膜成長用基板としても適する。

【0025】次に、本発明のSi基板表面処理方法について説明する。

【0026】まず、Si単結晶基板上にSi酸化物層を形成する。このSi酸化物層の形成は、基板表面が清浄化されたSi単結晶基板を真空槽中に配置し、酸化性ガスを導入しつつ加熱して行ういわゆる熱酸化法により行うことが好ましい。清浄化されたSi単結晶基板の基板表面は、上記したように極めて反応性に富むため、これを保護膜として用い、Si単結晶基板表面を再配列、汚

染などから保護する。Si単結晶基板の基板表面としては、(100)面を用いることが好ましい。上記Si酸化物層の層厚は、0.2~10nm程度、特に0.5~10nmとすることが好ましい。0.2nm未満ではSi表面の保護が不完全であるからである。上限を10nmとした理由は、後述する。

【0027】この工程によるSi酸化物層の形成において、後の工程でSi酸化膜を除去するためSi酸化物膜は薄く、かつSi基板結晶を保護する必要があるため連続したSi酸化膜でなくてはならない。

【0028】そのため、上記方法が望ましい。他の方法、たとえば自然酸化膜による方法、スパッタリングによるSi酸化物の形成では、膜厚が薄い時アイランド状に膜が形成されるため、Si基板結晶の保護が不完全になる場合がある。

【0029】上記酸化性ガスとしては、酸素、オゾン、原子状酸素、NO₂等を用いることができる。例えば、酸化性ガスとして酸素を用いる場合、この酸素の導入は、真空槽内を当初 $1 \times 10^{-7} \sim 1 \times 10^{-4}$ Torr程度の真空にし、酸素の導入により、少なくともSi単結晶基板の近傍の雰囲気圧が 1×10^{-4} Torr以上となるようにして行うことが好ましい。この雰囲気圧の酸素分圧の上限は特になく、純酸素や空気であってもよいが、好ましくは 1×10^{-1} Torr程度以下がよい。

【0030】上記の加熱は、300~700℃、特に500~700℃の温度に、0~10分程度保持して行うことが好ましい。このとき、昇温速度は、30~70℃/分程度とすることが好ましい。温度が高すぎたり、昇温速度が早すぎると、Si酸化膜の形成が不十分になり、逆に温度が低すぎたり、保持時間が長すぎると、Si酸化膜が厚すぎてしまう。

【0031】Si酸化物層の形成は、上記熱酸化法その他、SiO₂をターゲットと用いてのスパッタ法や、蒸着法等によって行うことができるが、前述したように薄く、連続した保護膜が好ましい。

【0032】上記工程後、さらに真空中で所定の温度に加熱する。Si表面結晶は、保護膜により、保護されているので、残留ガスである炭化水素と反応してSiC膜が形成される等の汚染がない。

【0033】加熱温度は、600℃から1200℃、好ましくは700℃から1100℃とすることが望ましい。600℃未満であると、後述する1×1構造が得られなくなることがある。1200℃以上であると、保護膜およびSiの蒸発により、Si結晶は乱れてしまうことがある。

【0034】ついで、アルカリ土類金属、希土類(Sc、Yを含む)、Zr、Hfの少なくとも1種類の金属と酸化性ガスとを表面に供給する。この過程で金属は、前工程で形成したSi酸化物による保護膜を還元し、除去する。同時に露出したSi表面結晶表面にアルカリ土

類金属、希土類(Sc、Yを含む)、Zr、Hfの少なくとも1種類の金属と酸素により、1×1の表面構造が形成される。酸化性ガスとしては、上記のものをを用いることができる。

【0035】金属の供給量は、アルカリ土類金属、希土類(Sc、Yを含む)、Zr、Hfの酸化物換算で、単位面積あたり0.3~10nm、特に3~7nm程度が好ましい。0.3nm未満では、Si酸化物の還元の効果が十分に発揮できず、10nmを超えると表面に原子レベルの凹凸が発生し易くなり、表面の結晶の配列は、凹凸により、1×1構造でなくなるためである。なお、上記Si酸化物層の層厚の上限の好ましい値を10nmとした理由は、10nmを超えると、上記のように金属を供給してもSi酸化物層を十分に還元できなくなる可能性があるのである。なお、表面には前記の金属の供給量に応じた金属と酸素を含む層が形成されていると考えられる。

【0036】酸化性ガスの導入は、酸素を用いるとき、少なくとも基板近傍の雰囲気圧の酸素分圧が $1 \times 10^{-4} \sim 1 \times 10^{-1}$ Torr程度となるようにすることが好ましい。最適酸素供給量は、真空槽の大きさ、ポンプの排気速度その他の要因で決まり、あらかじめ最適な流量を求めておくことがよく、2~50cc/分程度供給することが好ましい。

【0037】以上のようにして得られたSi表面処理基板は、この基板上に結晶性、表面性の優れた上述した酸化物エピタキシャル膜等が再現よく製造することが可能になる。

【0038】

【実施例】以下、本発明の具体的実施例を示し、本発明をさらに詳細に説明する。

【0039】Si単結晶基板として、その表面が(100)面となるように切断、鏡面研磨したSi単結晶を用いた。鏡面表面は購入後40%フッ化アンモニウム水溶液により、エッチング洗浄を行った。なお、上記単結晶基板は、直径2インチの円形基板を用いた。

【0040】真空槽内に設置された回転および加熱機構を備えた基板ホルダーに上記単結晶基板を固定し、真空蒸着槽を 10^{-6} Torrまで油拡散ポンプにより排気した後、基板近傍の雰囲気圧の酸素分圧を 10^{-2} Torr程度にするため、酸素を10cc/分の流量で導入し、この状態を工程終了まで維持した。基板を回転させ、600℃に加熱した。回転数は、20rpmとした。ここで、5分間保持し、Si表面にSi酸化物による保護膜を形成した。その膜厚は0.8nmであった。その後、その状態で基板温度を900℃に加熱した。ついで、実施例1としてSr(アルカリ土類金属)を、実施例2としてGd(希土類金属)を、実施例3として金属Zrを、実施例4として金属Hfを、実施例5としてSrとZrを量比(重量比)1:1でそれぞれ蒸発源からこれらそれぞれの金属

酸化物の膜厚に換算して5nm供給し、1×1の表面構造を備える実施例1ないし5のSi表面処理基板をそれぞれ得た。

【0041】これら実施例1ないし5のSi表面処理基板について表面を測定したRHEED像を図2ないし6に示す。これらは電子線の入射方向[110]で測定したものであるが、入射方向[1-10]で測定しても全く同じパターンであった。図7は比較のための、本発明の処理を施さない2×1構造のSi表面、図8は上記加熱温度を200℃としたときのRHEEDパターンであり、表面が乱れたSi表面のRHEED像を示す。図7では2×1の大きな単位メッシュをもつ複雑な超構造のパターンが現れている。図8では、SiCによる反射パターンが観察され、Si表面が汚染されSi結晶表面が乱れていることがわかる。本発明による図2から6のRHEEDパターンには超構造、SiCによる汚染などはみられず1×1のストリークパターンのみが観察され、安定な1×1の表面構造をしたSi表面処理基板が得られていることが確認される。

【0042】本発明によるSi表面処理基板上、例として図4で示したZrを用いたSi処理基板に、誘電体材料であるYSZを蒸着法によりエピタキシャル成長させた膜表面のRHEEDパターンを図9に示す。回折パターンはシャープでストリーク状になっていることから、YSZ誘電体膜は単結晶で、その表面は平坦であることがわかる。前述した、比較例による、Si上のYSZエピタキシャル膜のRHEEDパターンと比較して、極端にストリーク性が強い。従来のYSZのエピタキシャル膜の結晶性および表面性が本発明の効果により、大きく改善されている。なお、Sr以外のアルカリ土類金属およびGd以外の希土類金属についても同様の実験を行ったところ、Si単結晶基板上にそれらの金属と酸素により形成された1×1の表面構造が得られた。また、これらの1×1の表面構造を有するSi基板および実施例1、2、4、5のSi基板を用いて、その基板表面上にYSZを成長させたところ、上記と同様に良好なエピタキシャル膜が得られた。

【0043】

【発明の効果】以上説明したように、本発明によるSi表面処理基板は、本発明のSi表面処理基板は、Si表面がアルカリ土類、希土類（Sc、Yを含む）、Zr、Hfの少なくとも1種類の金属と酸素により形成された1×1の表面構造を有している。この表面ではSi表面の構造が安定で、かつ結晶構造情報を成長させる酸化物膜へ伝える役割を果たす。この基板をもちいると、この基板上に結晶性、表面性の優れた酸化物エピタキシャル

膜が再現よく製造することが可能になり、工業的に極めて利用価値の高いものである。

【図面の簡単な説明】

【図1】(a)は、1×1の表面構造のRHEEDパターンを示す模式図であり、(b)は、2×1、1×2、あるいはこれらが混合している場合の表面構造のRHEEDパターンを示す模式図である。

【図2】Sr金属と酸素により形成された1×1の表面構造を有する本発明の実施例1のSi基板の表面結晶構造を示す図面代用写真であって、RHEEDパターンを示すものであり、Si単結晶基板の[110]方向から電子線を入射した場合の回折パターンである。

【図3】Gd金属と酸素により形成された1×1の表面構造を有する実施例2のSi基板の表面結晶構造を示す図面代用写真であって、RHEEDパターンを示すものであり、Si単結晶基板の[110]方向から電子線を入射した場合の回折パターンである。

【図4】Zr金属と酸素により形成された1×1の表面構造を有する実施例3のSi基板の表面結晶構造を示す図面代用写真であって、RHEEDパターンを示すものであり、Si単結晶基板の[110]方向から電子線を入射した場合の回折パターンである。

【図5】Hf金属と酸素により形成された1×1の表面構造を有する実施例4のSi基板の表面結晶構造を示す図面代用写真であって、RHEEDパターンを示すものであり、Si単結晶基板の[110]方向から電子線を入射した場合の回折パターンである。

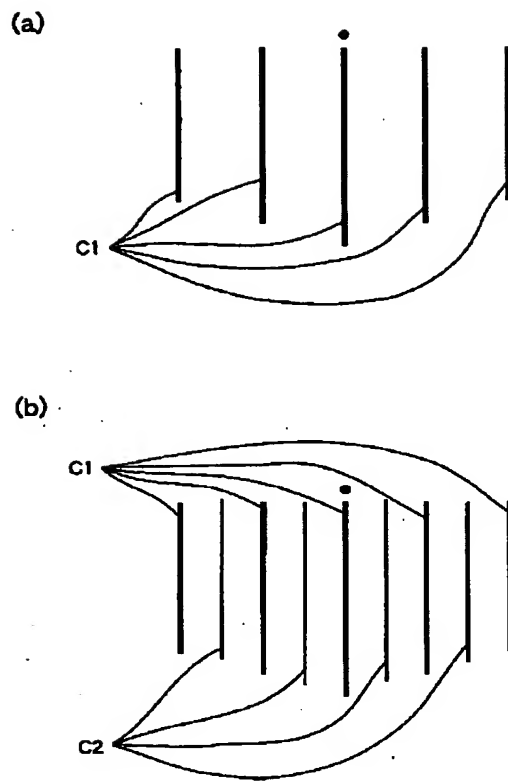
【図6】Sr金属とZr金属と酸素により形成された1×1の表面構造を有する実施例5のSi基板の表面結晶構造を示す図面代用写真であって、RHEEDパターンを示すものであり、Si単結晶基板の[110]方向から電子線を入射した場合の回折パターンである。

【図7】本発明の処理を施さない比較例の2×1構造のSi基板表面の表面結晶構造を示す図面代用写真であって、RHEEDパターンを示すものであり、Si単結晶基板の[110]方向から電子線を入射した場合の回折パターンである。

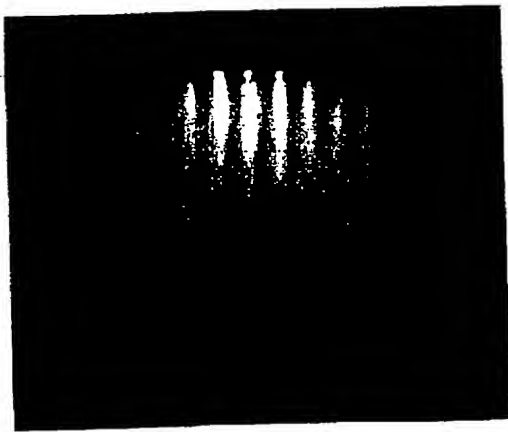
【図8】Siの形成を200℃で行った場合の他の比較例によるSi基板表面の表面結晶構造を示す図面代用写真であって、表面が乱れたSi表面のRHEED像を示すSi単結晶基板の[110]方向から電子線を入射した場合の回折パターンである。

【図9】本発明のSi基板を用いて、誘電体薄膜であるYSZをエピタキシャル成長させた膜表面のRHEEDパターンであり、Si単結晶基板の[110]方向から電子線を入射した場合の回折パターンである。

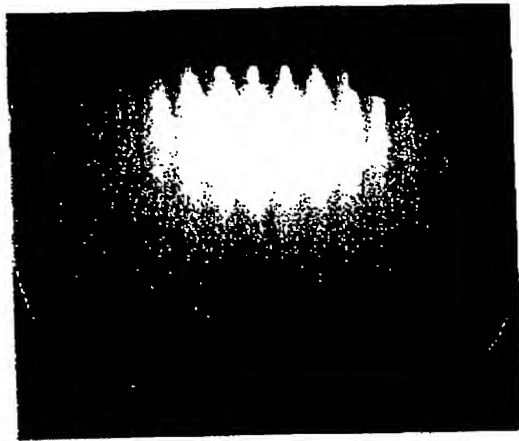
【図1】



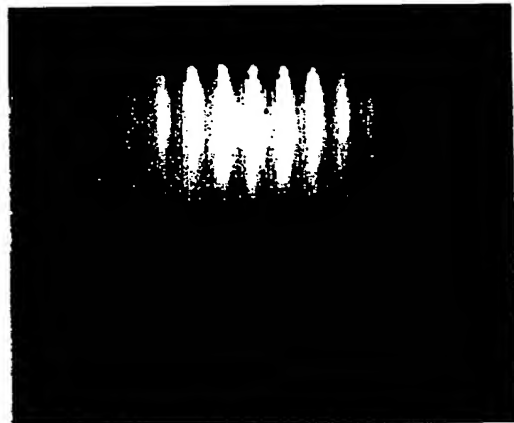
【図3】



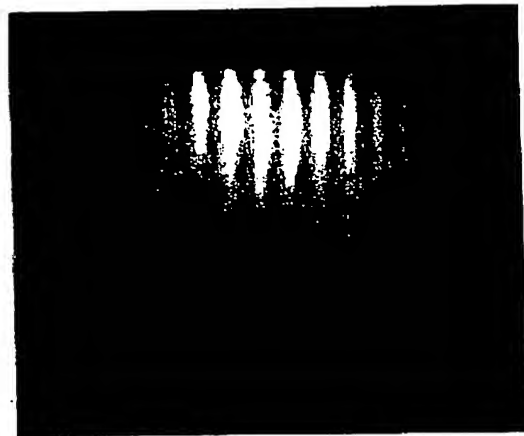
【図2】



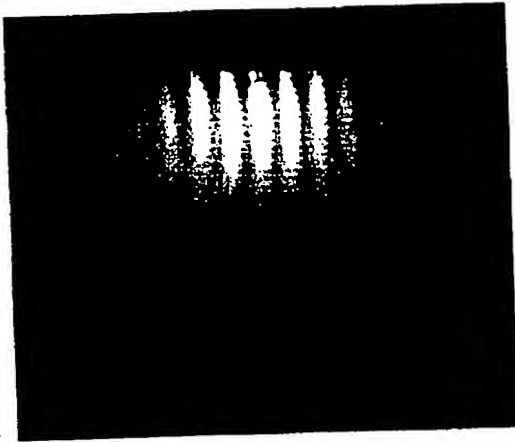
【図4】



【図5】



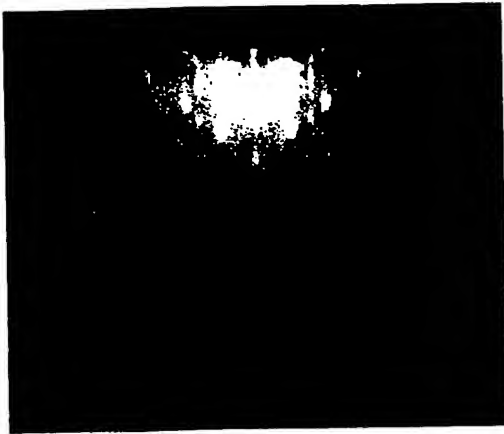
【図6】



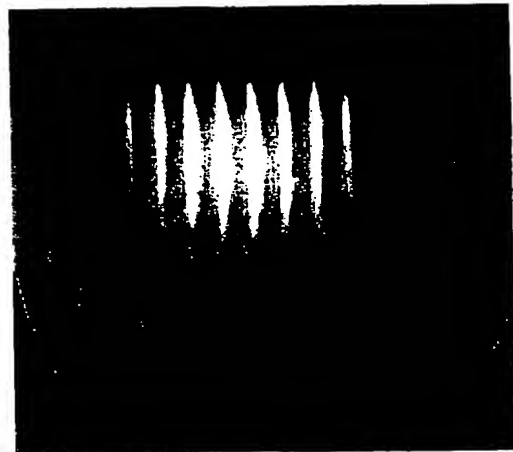
【図7】



【図8】



【図9】



【手続補正書】

【提出日】平成7年9月14日

【手続補正1】

【補正対象書類名】図面

【補正対象項目名】図2

【補正方法】変更

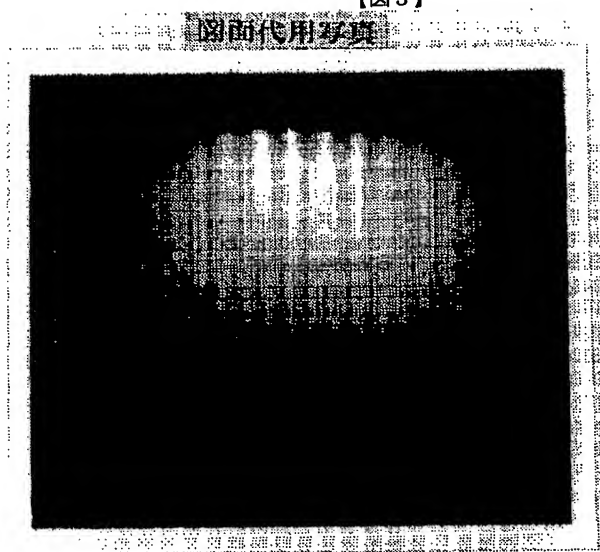
【補正内容】

【図2】



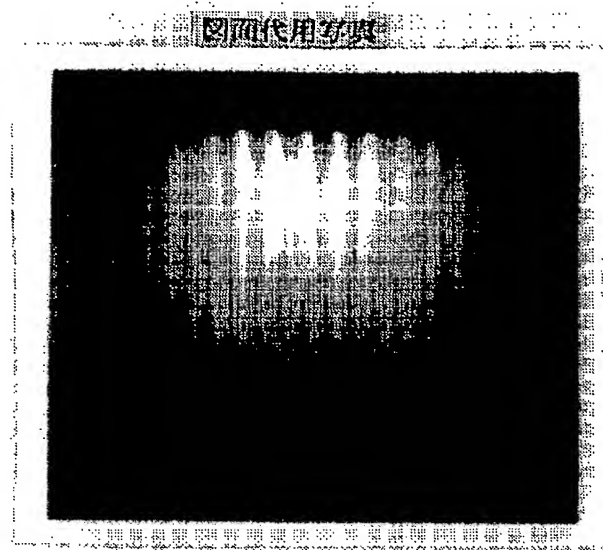
【手続補正2】
 【補正対象書類名】図面
 【補正対象項目名】図3

【補正方法】変更
 【補正内容】
 【図3】



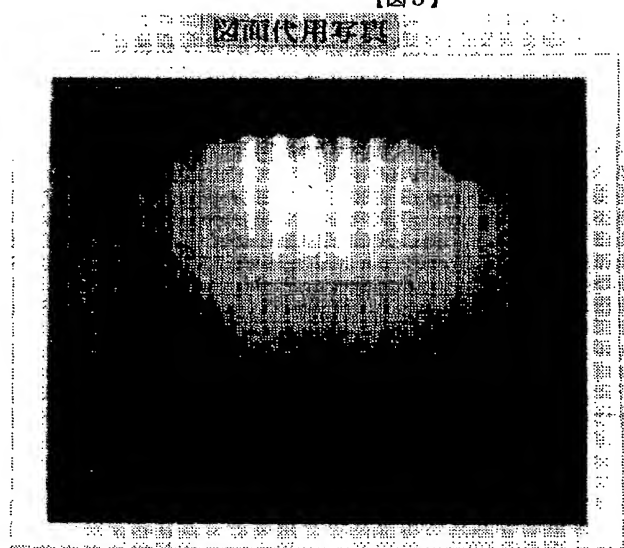
【手続補正3】
 【補正対象書類名】図面
 【補正対象項目名】図4

【補正方法】変更
 【補正内容】
 【図4】



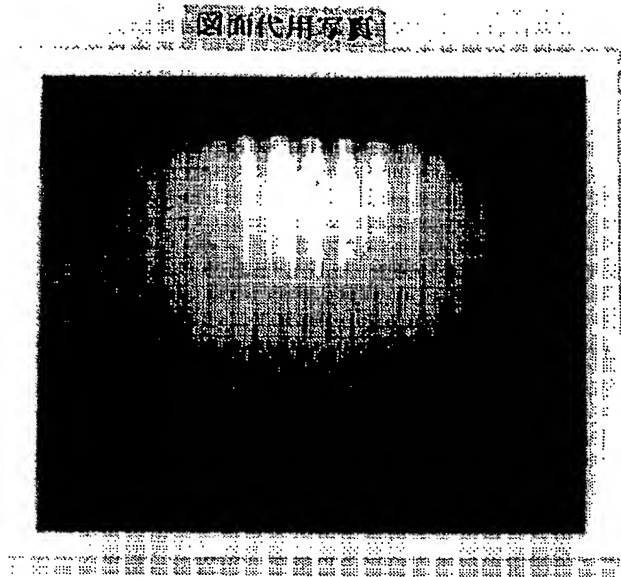
【手続補正4】
【補正対象書類名】図面
【補正対象項目名】図5

【補正方法】変更
【補正内容】
【図5】



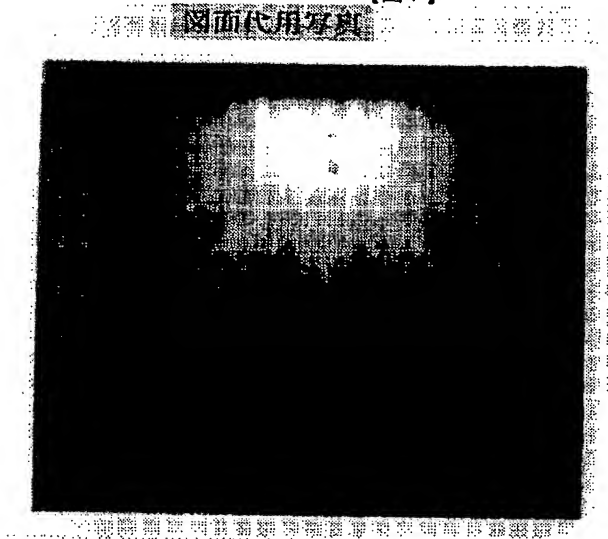
【手続補正5】
【補正対象書類名】図面
【補正対象項目名】図6

【補正方法】変更
【補正内容】
【図6】



【手続補正6】
 【補正対象書類名】図面
 【補正対象項目名】図7

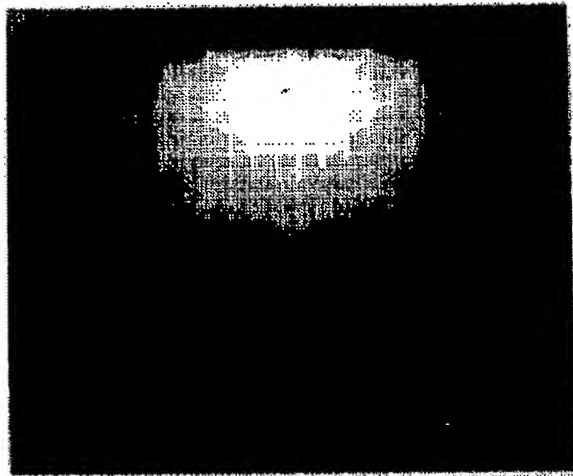
【補正方法】変更
 【補正内容】
 【図7】



【手続補正7】
 【補正対象書類名】図面
 【補正対象項目名】図8

【補正方法】変更
 【補正内容】
 【図8】

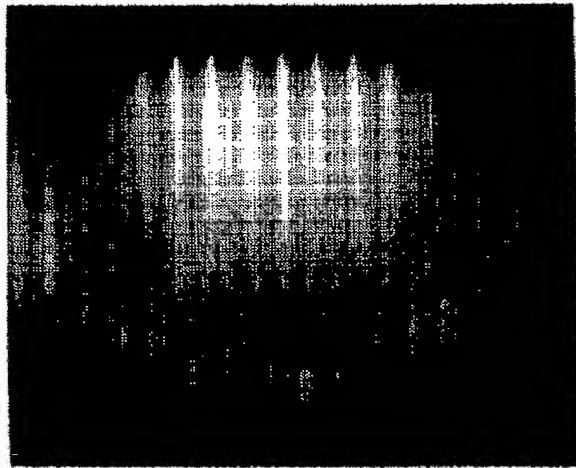
図面代用写真



【手続補正 8】
【補正対象書類名】図面
【補正対象項目名】図 9

【補正方法】変更
【補正内容】
【図 9】

図面代用写真



フロントページの続き

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39/24

技術表示箇所

Z A A B
Z A A B

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

 CLAIMS

[Claim(s)]

[Claim 1] Si substrate in which it consists of Si single crystals and the substrate front face has the surface structure of 1x1 formed of an alkaline earth, rare earth (Sc and Y are included), and at least one kind of metal and oxygen of Zr and Hf.

[Claim 2] Forming Si oxide layer in Si single crystal substrate front face, and heating in a vacuum after this Alkaline earth metal, rare earth (Sc and Y are included), and at least one kind of metal and the oxidizing gas of Zr and Hf are supplied to a front face. The surface treatment method of Si substrate characterized by making a substrate front face into the surface structure of 1x1 formed of an alkaline earth, rare earth (Sc and Y are included), and at least one kind of metal and oxygen of Zr and Hf.

[Claim 3] the inside of the vacuum tub which introduced the oxidizing gas when forming the aforementioned Si oxide layer -- Si single crystal substrate -- 300-700 degrees C -- heating -- the surface treatment method of Si substrate of the claim 2 in a vacuum tub which sets the oxygen tension of the atmosphere near the substrate to 1×10^{-4} to 4 or more Torrs at least, and forms 0.2-10nm Si oxide layer

[Claim 4] The metaled evaporation made into the purpose performs supply of the aforementioned metal, in the case of this evaporation, the substrate temperature of Si single crystal substrate is set as 600 degrees C - 1200 degrees C, a oxidizing gas is introduced in this state, and it is the Si substrate surface treatment method of the claims 2 or 3 in a vacuum tub which set atmosphere near the Si single crystal substrate to 1×10^{-4} - 1×10^{-1} Torr at least.

[Claim 5] One Si substrate surface treatment method of the claims 2-4 which use the aforementioned Si single crystal substrate so that the (100) field may turn into a substrate front face.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the surface treatment method especially used for a process sensitive to the structure of the surface layer of a substrate, the substrate for epitaxial growth of oxide thin films, such as a high dielectric constant thin film to Si substrate top, a ferroelectric thin film, and a superconductivity thin film, and substrate pretreatment before an epitaxial growth process about Si substrate and its surface treatment method.

[0002]

[Description of the Prior Art] A semiconductor device, for example, the gate in SiFET used in DRAM, is usually polycrystal or an amorphous silicon O₂ as an oxide film. A film is used and the MOS structure is constituted. Integration follows on progressing, a smaller thing is required and the size of an MOS capacitor is coming to the limitation by the present degree of integration. SiO₂ A dielectric constant is the dielectric which has a still bigger dielectric constant in order to be about 3 and to secure the charge for working the gate of FET with an MOS capacitor SiO₂ It must use instead and a good MOS property must be acquired. SiO₂ With Si, since it is congenial, it has been used for Si device in the state of [amorphous] polycrystal. However, SiO₂ It is difficult to secure the optimal device property and its repeatability in the state of [amorphous] polycrystal with substitute other material. The disturbance of the physical quantity by the grain boundary in the polycrystalline substance and the instability of the material physical-properties value in an amorphous state are considered to be the main causes, and it is SiO₂. The present condition is that substitute other material is not actually used for Si device.

[0003] Therefore, SiO₂ Instead, with the single crystal, a dielectric constant is large and the dielectric thin film material which was excellent in the MOS (MIS) property is needed. By development of this dielectric thin film, it becomes realizable [the dielectric separation IC by still higher LSI of a degree of integration, and SOI technology etc. / a SOI device].

[0004] Moreover, the electron device which formed the ferroelectric film or the superconductivity film on Si substrate which is a semiconducting-crystal substrate, and was integrated is devised. By combining a semiconductor, a superconductor, or a ferroelectric, a nonvolatile memory, an infrared sensor, an optical modulator, optical-switch OEIC (opto-electronic integrated circuit : opto-electronic integrated circuits), etc. are made as an experiment in the combination of a semiconductor and a superconductor with semiconductors, such as SQUID, a Josephson device, a superconductivity transistor, an electromagnetic wave sensor, and the superconductivity wiring LSI, and the ferroelectric.

[0005] In the semiconductor device using these superconductors material or ferroelectric material, in order to secure the optimal device property and its repeatability, it is required to use a single crystal as superconductor material and dielectric materials. In the polycrystalline substance, it is difficult to obtain a good device property because of the disturbance of the physical quantity by the grain boundary. This is the same also about a thin film material, and the superconductivity near the most perfect possible single crystal or a dielectric epitaxial film is desired.

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[0007] Moreover, the method of carrying out a crystal growth on Si substrate is examined also about oxides superconductors and the ferroelectric. The crystal structure of the main oxides superconductors and ferroelectrics which are applicatively worthy has taken the perovskite structure. Now, it is impossible for epitaxial growth of a perovskite type oxide to be greatly dependent on the material and crystal orientation of a substrate, and to grow a perovskite type oxide epitaxially directly to up to Si substrate. Then, it is Appl.Phys.Lett., Vol.54, No.8, p.754-p.756 (1989), and Japanese that you prepare the buffer layer which grew epitaxially to Si, and a perovskite type oxide makes it grow epitaxially on it. Journal of Applied Physics, Vol.29, No.9, L955-57 (1990), and JP,2-82585,A.

[0008] The crystal growth of the oxide epitaxial film of such a dielectric and a superconductor, and a ferroelectric is carried out on Si substrate, and it is processed according to semiconductor processes, such as electrode formation and micro processing. By combining a semiconductor device and an oxide epitaxial film, SOI devices, such as the dielectric separation IC by still higher LSI and SOI technology, SQUID, the Josephson device, the superconductivity transistor, the electromagnetic wave sensor and the superconductivity wiring LSI, a nonvolatile memory, an infrared sensor, an optical modulator, optical-switch OEIC, etc. of a degree of integration can be manufactured. Since the epitaxial film of an oxide does not have the disturbance of physical quantity, such as a grain boundary, it demonstrates a good function by each application.

[0009] In the front face of Si single crystal, it is SiO_2 in air. The natural oxidation film is formed. If this natural oxidation film exists, the crystal information on Si substrate will not get across to a film, but epitaxial growth will become impossible.

[0010] Then, by the above-mentioned method, processing for acquiring the pure side of Si is performed first.

[0011] It etches as a method, rotating a substrate. A substrate is rotated in nitrogen-gas-atmosphere mind, and a rinse is carried out in high grade alcohol. Then, the solution of HF of a high grade, ethanol, and pure water (1:10:1) is dropped altogether, and it *****s. This substrate is put into the glove box of nitrogen-gas-atmosphere mind, and is transported, and membrane formation equipment is equipped quickly. Furthermore, a vacuum tub is made into the temperature which exhausts to the high vacuum of 1×10^{-6} or more Torr, heats, and forms membranes. In order to prevent contamination on the front face of a substrate at this process, it is made to keep the inside of a vacuum tub as pure as possible. In an above-mentioned example, a ***** Si substrate is used for epitaxial growth in cautions in this way, and the process is very complicated. Moreover, the method of inserting an interface control layer as other methods, in order to pull out the crystal information on Si in early stages of membranous growth is Japanese. Journal of Applied Physics, Vol.30, and L1415-1417 (1991). also in this method, processing conditions are alike, and it is sensitive, and is complicated and is [epitaxial growth of an oxide is realized only by the optimal processing, and] lacking in repeatability

[0012] Moreover, generally the elevated temperature of 700 degrees C or more is required for epitaxial

growth of an oxide. Si front face which it defecated as mentioned above is rich in reactivity, it is 700 degrees C or more in the above-mentioned temperature, and residual gas especially a hydrocarbon, and a reaction are caused in a vacuum, by forming SiC in a front face, a substrate front face is polluted and the crystal on the front face of a substrate is confused. On disordered Si substrate front face, crystal information does not get across to a film enough, but epitaxial growth becomes impossible.

[0013]

[Problem(s) to be Solved by the Invention] Then, on the occasion of epitaxial growth of an oxide, it is a membrane formation temperature field and this invention aims at offering Si substrate which plays the role told to the oxide film into which the structure on the front face of Si is stable, and crystal structure information is grown up, is reproducible, and is excellent in mass-production nature, and its surface treatment method.

[0014]

[Means for Solving the Problem] Such a purpose is attained by this invention of following the (1) - (5).

(1) Si substrate in which it consists of Si single crystals and the substrate front face has the surface structure of 1x1 formed of an alkaline earth, rare earth (Sc and Y are included), and at least one kind of metal and oxygen of Zr and Hf.

(2), forming Si oxide layer in Si single crystal substrate front face, and heating in a vacuum after this Alkaline earth metal, rare earth (Sc and Y are included), and at least one kind of metal and the oxidizing gas of Zr and Hf are supplied to a front face. The surface treatment method of Si substrate characterized by making a substrate front face into the surface structure of 1x1 formed of an alkaline earth, rare earth (Sc and Y are included), and at least one kind of metal and oxygen of Zr and Hf.

(3) the inside of the vacuum tub which introduced the oxidizing gas when forming the aforementioned Si oxide layer -- Si single crystal substrate -- 300-700 degrees C -- heating -- the surface treatment method of Si substrate the above in a vacuum tub (2) which sets the oxygen tension of the atmosphere near the substrate to 1×10^{-4} to 4 or more Torrs at least, and forms 0.2-10nm Si oxide layer

(4) evaporation of the metal which targets supply of the aforementioned metal -- carrying out -- the time of this evaporation -- the substrate temperature of Si single crystal substrate -- 600 degrees C - 1200 degrees C -- setting up -- this state -- a oxidizing gas -- introducing -- the above in a vacuum tub (2) which sets atmosphere near the Si single crystal substrate to 1×10^{-4} - 1×10^{-1} Torr at least, or the Si substrate surface treatment method of (3)

(5) One Si substrate surface treatment method of above-mentioned (2) - (4) which uses the aforementioned Si single crystal substrate so that the (100) field may turn into a substrate front face.

[0015]

[Function and Effect of the Invention] Si substrate by this invention has the surface structure of 1x1 in which the substrate front face was formed of an alkaline earth, rare earth (Sc and Y are included), and at least one kind of metal and oxygen of Zr and Hf in view of Si front face being rich [reactivity], and unstable, without exposing the crystal front face of Si. Moreover, on the occasion of epitaxial growth of an oxide, it is flat and a crystal front face with sufficient periodicity appears, and this front face is a membrane formation temperature field, and since structure is stable, it tells crystal structure information good to the oxide film to grow up. By using this substrate, it becomes possible to manufacture the oxide epitaxial film which was excellent in crystallinity and front-face nature on this substrate with sufficient repeatability. Since especially the surface structure of the substrate considered in an oxide epitaxial film crystal when the bulk crystal structure is cut turns into 1x1 structure, it is thought that it becomes possible to perform [make / make / it] epitaxial growth good also from this point.

[0016]

[Elements of the Invention] Si substrate of this invention consisted of Si single crystals, and the substrate front face was formed of an alkaline earth, rare earth (Sc and Y are included), and at least one kind of metal and oxygen of Zr and Hf -- it has the surface structure of 1x1 substantially

[0017] The pattern of the image by the reflective high-speed electron diffraction (RHEED is called below Reflection High Energy Electron Diffraction :) can investigate a surface structure. For example, when this invention is the surface structure of 1x1 made into the purpose, the direction of electron ray

incidence serves as a perfect streak pattern of the 1 time period C1 as shown in (a) of drawing 1 by [110], and serves as the pattern completely same as for [1-10] in the direction of incidence. On the other hand, Si single crystal clean surface serves as 1x2, 2x1, or 1x1 and the surface structure in which 2x1 is intermingled. In such a case, the pattern of a RHEED image turns into a pattern with the 1 time period C1 as shown in (b) of drawing 1 by the direction of incidence of an electron ray [110], either of [1-10], or both, and the double-precision period C2. the surface structure of 1x1 of this invention -- setting -- the pattern of Above RHEED -- seeing -- the direction of incidence -- [110] and [1-10] -- it is both and the double-precision period C2 of (b) of drawing 1 is not seen. In addition, the information on the thickness about a front face 1 - a number atom is acquired from RHEED.

[0018] Moreover, Si clean surface may show 1x1 structure. The thing with the conditions indefinite although our experiment was also observed several times which show 1x1 acquired with stably sufficient repeatability for 1x1 in respect of Si pure is impossible in the present condition.

[0019] 1x2, 2x1, and 1x1 -- it is easy to be polluted with an elevated temperature among a vacuum, and Si pure side of which structure reacts with the hydrocarbon contained especially in residual gas, and forms SiC in a front face, and the crystal on the front face of a substrate is confused. Therefore, the former was impossible for forming stably 1x1 structure where it was suitable when carrying out the crystal growth of the oxide film on Si substrate.

[0020] The front face which shows the surface structure of 1x1 of this invention is formed of the interaction of M, oxygen, and Si in the above-mentioned alkaline earth, rare earth (Sc and Y are included), and at least one kind of metal of Zr and Hf. Without being polluted in an elevated temperature and a vacuum, this front face is stable and the optimal as a substrate to which the crystal growth of the oxide is carried out.

[0021] The quantitative ratio when using two or more sorts out of the above as a metal M is arbitrary.

[0022] In addition, the above-mentioned alkaline earth metal shows Calcium calcium, Strontium Sr, Barium Ba, Radium Ra, Beryllium Be, and Magnesium Mg. Moreover, the rare earth metal shows Yttrium Y, Lanthanum La, Cerium Ce, Praseodymium Pr, Neodymium Nd, Promethium Pm, Samarium Sm, Europium Eu, Gadolinium Gd, Terbium Tb, Dysprosium Dy, Holmium Ho, Erbium Er, Thulium Tm, Ytterbium Yb, Lutetium Lu, and Scandium Sc.

[0023] Si substrate of this invention -- the substrate front face -- composition $Zr_{1-x}R_xO_{2-\delta}$ (the rare earth metal in which it is here and R contains Y -- it is -- $x=0-0.75$ -- it is 0.2-0.50 preferably) Moreover, δ is usually 0-0.5. And epitaxial films, such as a perovskite, can be grown good.

[0024] With the epitaxial film which has the above-mentioned perovskite structure Specifically High-temperature superconductivity films, such as Bi system oxide superconductivity film and a $YBa_2Cu_3O_{7-8}$ superconductivity (YBCO) film, Ferroelectric films, such as $BaTiO_3$, $PbTiO_3$, PZT, PLZT, other Pb system perovskites, other Bi system perovskites, and Bi stratified compound, and a further $La_{1-x}Sr_xCoO_3$ and $La_{1-x}Sr_xCa_xRuO_3$ etc. -- an oxide electric conduction film is mentioned. Moreover, it is suitable also as a substrate for film growth of semiconductors, such as In_2O_3 (Sn dope), other oxide electric conduction films, Pt, Si and germanium, and GaAs, or metal.

[0025] Next, the Si substrate surface treatment method of this invention is explained.

[0026] First, Si oxide layer is formed on Si single crystal substrate. It is desirable to perform formation of this Si oxide layer by the so-called oxidizing [thermally] method which arranges Si single crystal substrate which defecated the substrate front face in a vacuum tub, heats, introducing a oxidizing gas, and is performed. Since the substrate front face of Si single crystal substrate which it defecated is extremely rich in reactivity as described above, it protects Si single crystal substrate front face from a rearrangement, contamination, etc., using this as a protective coat. As a substrate front face of Si single crystal substrate, it is desirable to use a field (100). As for especially the thickness of the above-mentioned Si oxide layer, it is desirable to be referred to as 0.5-10nm about 0.2-10nm. 0. In less than 2nm, it is because protection of Si front face is imperfect. The reason for having set the upper limit to 10nm is mentioned later.

[0027] In formation of Si oxide layer by this process, in order to remove Si oxide film at a next process, Si oxide film must be thin, and you must be Si oxide film which continued since it was necessary to

protect Si substrate crystal.

[0028] Therefore, the above-mentioned method is desirable. In formation of other methods, for example, the method by the natural oxidation film, and Si oxide by sputtering, since a film is formed in the shape of an island when thickness is thin, protection of Si substrate crystal may become imperfect.

[0029] as the above-mentioned oxidizing gas -- oxygen, ozone, atom-like oxygen, and NO₂ etc. -- it can use For example, when using oxygen as a oxidizing gas, it is desirable for introduction of this oxygen to make the inside of a vacuum tub the vacuum of about 1×10^{-7} to 1×10^{-4} Torr at the beginning, and to perform it by [as setting the atmosphere near the Si single crystal substrate to 1×10^{-4} to 4 or more Torr at least] by introduction of oxygen. Although there may not be especially an upper limit of the oxygen tension of this atmosphere and you may be pure oxygen and air, about 1×10^{-4} to 1 or less Torr is preferably good.

[0030] It is desirable to hold especially the above-mentioned heating to the temperature of 500-700 degrees C about 0 to 10 minutes, and to perform it to it 300-700 degrees C. As for a programming rate, at this time, it is desirable to carry out in about 30-70 degrees C/minute. If temperature is too high, or formation of Si oxide film will become inadequate if a programming rate is too early, and the holding time is too long in temperature being too low conversely, Si oxide film will be too thick.

[0031] Formation of Si oxide layer is SiO₂ besides the above-mentioned oxidizing [thermally] method. Although it can carry out by the target, a spatter, a vacuum deposition to be used, etc., as mentioned above, it is thin and the continuous protective coat is desirable.

[0032] It heats to temperature predetermined in the inside of a vacuum further after the above-mentioned process. Since Si surface crystal is protected by the protective coat, it reacts with the hydrocarbon which is residual gas, and does not have contamination of a SiC film being formed.

[0033] As for heating temperature, it is desirable to make 1200 degrees C into 700 to 1100 degrees C preferably from 600 degrees C. If it is less than 600 degrees C, 1×1 structure mentioned later may not no longer be acquired. When it is 1200 degrees C or more, Si crystal may be confused by evaporation of a protective coat and Si.

[0034] Subsequently, alkaline earth metal, rare earth (Sc and Y are included), and at least one kind of metal and the oxidizing gas of Zr and Hf are supplied to a front face. A metal returns and removes the protective coat by Si oxide formed at the last process in this process. The surface structure of 1×1 is formed in Si surface crystal front face exposed simultaneously of alkaline earth metal, rare earth (Sc and Y are included), and at least one kind of metal and oxygen of Zr and Hf. The above-mentioned thing can be used as a oxidizing gas.

[0035] The metaled amount of supply is alkaline earth metal, rare earth (Sc and Y are included), and oxide conversion of Zr and Hf, and its about 3-7nm is especially desirable 0.3-10nm per unit area. 0. if the effect of reduction of Si oxide cannot fully demonstrate but exceeds 10nm in less than 3nm -- a front face -- the irregularity of atomic level -- generating -- being easy -- the array which is a surface crystal is because it is no longer 1×1 structure by irregularity In addition, the reason for having set the desirable value of the upper limit of the thickness of the above-mentioned Si oxide layer to 10nm is that possibility that it becomes impossible to fully return Si oxide layer will come out even if it supplies a metal as mentioned above if it exceeds 10nm. In addition, it is thought that the layer containing the aforementioned metaled metal according to the amount of supply and aforementioned metaled oxygen is formed in a front face.

[0036] When using oxygen, as for introduction of a oxidizing gas, it is desirable to make it the oxygen tension of the atmosphere near the substrate set to about 1×10^{-4} to 1×10^{-1} Torr at least. As for the optimal oxygen supply, it is good for it to be decided by the size of a vacuum tub and the factor of a pumping speed and others, and to calculate the optimal flow rate beforehand, and it is desirable to supply about 2-50cc /a minute.

[0037] It enables the oxide epitaxial film which was excellent in crystallinity and front-face nature on this substrate and which was mentioned above to manufacture Si surface treatment substrate obtained as mentioned above with sufficient reappearance.

[0038]

[Example] Hereafter, the concrete example of this invention is shown and this invention is further explained to a detail.

[0039] As an Si single crystal substrate, cutting and Si single crystal which carried out mirror polishing were used so that the front face might turn into a field (100). The mirror-plane front face performed etching washing by ammonium-fluoride solution after [purchase] 40%. In addition, the circular substrate with a diameter of 2 inches was used for the above-mentioned single crystal substrate.

[0040] After fixing the above-mentioned single crystal substrate to the substrate electrode holder equipped with the rotation and the heating mechanism which were installed in the vacuum tub and exhausting a vacuum deposition tub with an oil diffusion pump to 10⁻⁶Torr, in order to set the oxygen tension of the atmosphere near the substrate to about 10 to 2 Torrs, oxygen was introduced by ten cc flow rate for /, and this state was maintained till the process end. The substrate was rotated and it heated at 600 degrees C. A rotational frequency is 20rpm. It carried out. Here, it held for 5 minutes and the protective coat by Si oxide was formed in Si front face. The thickness was 0.8nm. Then, substrate temperature was heated at 900 degrees C in the state. Sr (alkaline earth metal) as an example 2 as an example 1 subsequently, Gd (rare earth metal) As an example 4, convert Sr and Zr into the thickness of each metallic oxide of these from an evaporation source by the quantitative ratio (weight ratio) 1:1 as an example 5, respectively, and 5nm of metals Hf is supplied. as an example 3 -- Metal Zr -- An example 1 or Si surface treatment substrate of 5 equipped with the surface structure of 1x1 was obtained, respectively.

[0041] The RHEED image which measured the front face about these examples 1 or Si surface treatment substrate of 5 is shown in drawing 2 or 6. Although these were measured in the direction of incidence of an electron ray [110], even if measured in the direction of incidence [1-10], it was the completely same pattern. Si front face of 2x1 structure where drawing 7 does not process this invention for comparison, and drawing 8 are the RHEED patterns when making the above-mentioned heating temperature into 200 degrees C, and show the RHEED image on the front face of Si on which the front face was in disorder. In drawing 7, the complicated pattern with the big unit mesh of 2x1 of super-structure has appeared. It turns out that the reflective pattern by SiC is observed, Si front face is polluted with drawing 8, and Si crystal front face is in disorder. Super-structure, the contamination by SiC, etc. are not seen by the RHEED pattern of 6 from drawing 2 by this invention, but only the streak pattern of 1x1 is observed, and it is checked that Si surface treatment substrate which carried out the stable surface structure of 1x1 is obtained.

[0042] The RHEED pattern on the front face of a film which grew epitaxially YSZ which is dielectric materials into Si processing substrate using Zr shown by drawing 4 as an example by the vacuum deposition is shown in drawing 9 on Si surface treatment substrate by this invention. A diffraction pattern is sharp, and since it has become streak-like, a YSZ dielectric film is a single crystal and it turns out that the front face is flat. As compared with the RHEED pattern of the YSZ epitaxial film on Si by the example of comparison mentioned above, streak nature is extremely strong. The crystallinity of the epitaxial film of the conventional YSZ and front-face nature are a book. In addition, when the experiment with the same said of alkaline earth metal other than Sr and rare earth metals other than Gd was conducted, the surface structure of 1x1 formed of those metals and oxygen on Si single crystal substrate was obtained. Moreover, when YSZ was grown up on the substrate front face using Si substrate which has these surface structures of 1x1, and Si substrate of examples 1, 2, 4, and 5, the good epitaxial film was obtained like the above.

[0043]

[Effect of the Invention] As explained above, as for Si surface treatment substrate by this invention, Si front face has the surface structure of 1x1 formed of an alkaline earth, rare earth (Sc and Y are included), and at least one kind of metal and oxygen of Zr and Hf, as for Si surface treatment substrate of this invention. On this front face, the structure on the front face of Si is stable, and plays the role told to the oxide film into which crystal structure information is grown up. When it is with this substrate, the oxide epitaxial film which was excellent in crystallinity and front-face nature on this substrate is enabled to manufacture with sufficient reappearance, and utility value is industrial very high.

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 PRIOR ART

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[0009] In the front face of Si single crystal, it is SiO₂ in air. The natural oxidation film is formed. If this natural oxidation film exists, the crystal information on Si substrate will not get across to a film, but epitaxial growth will become impossible.

[0010] Then, by the above-mentioned method, processing for acquiring the pure side of Si is performed first.

[0011] It etches as a method, rotating a substrate. A substrate is rotated in nitrogen-gas-atmosphere mind, and a rinse is carried out in high grade alcohol. Then, the solution of HF of a high grade, ethanol, and pure water (1:10:1) is dropped altogether, and it *****s. This substrate is put into the glove box of nitrogen-gas-atmosphere mind, and is transported, and membrane formation equipment is equipped quickly. Furthermore, a vacuum tub is made into the temperature which exhausts to the high vacuum of 1x10 to 6 or more Torrs, heats, and forms membranes. In order to prevent contamination on the front face of a substrate at this process, it is made to keep the inside of a vacuum tub as pure as possible. In an above-mentioned example, a ***** Si substrate is used for epitaxial growth in cautions in this way, and the process is very complicated. Moreover, the method of inserting an interface control layer as other methods, in order to pull out the crystal information on Si in early stages of membranous growth is Japanese. Journal of Applied It is shown in Physics, Vol.30, and L1415-1417 (1991). also in this method, processing conditions are alike, and it is sensitive, and is complicated and is [epitaxial growth of an oxide is realized only by the optimal processing, and] lacking in repeatability

[0012] Moreover, generally the elevated temperature of 700 degrees C or more is required for epitaxial growth of an oxide. Si front face which it defecated as mentioned above is rich in reactivity, it is 700 degrees C or more in the above-mentioned temperature, and residual gas especially a hydrocarbon, and a reaction are caused in a vacuum, by forming SiC in a front face, a substrate front face is polluted and the crystal on the front face of a substrate is confused. On disordered Si substrate front face, crystal information does not get across to a film enough, but epitaxial growth becomes impossible.

[Translation done.]

* NOTICES *

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2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] (a) is the ** type view showing the RHEED pattern of the surface structure of 1x1, and (b) is the ** type view showing the RHEED pattern of a surface structure in case 2x1, 1x2, or these are being mixed.

[Drawing 2] It is the drawing substitution photograph in which the surface crystal structure of Si substrate of the example 1 of this invention which has the surface structure of 1x1 formed of Sr metal and oxygen is shown, and is a diffraction pattern at the time of a RHEED pattern being shown and carrying out [of Si single crystal substrate] incidence of the electron ray from [110].

[Drawing 3] It is the drawing substitution photograph in which the surface crystal structure of Si substrate of the example 2 which has the surface structure of 1x1 formed of Gd metal and oxygen is shown, and is a diffraction pattern at the time of a RHEED pattern being shown and carrying out [of Si single crystal substrate] incidence of the electron ray from [110].

[Drawing 4] It is the drawing substitution photograph in which the surface crystal structure of Si substrate of the example 3 which has the surface structure of 1x1 formed of Zr metal and oxygen is shown, and is a diffraction pattern at the time of a RHEED pattern being shown and carrying out [of Si single crystal substrate] incidence of the electron ray from [110].

[Drawing 5] It is the drawing substitution photograph in which the surface crystal structure of Si substrate of the example 4 which has the surface structure of 1x1 formed of Hf metal and oxygen is shown, and is a diffraction pattern at the time of a RHEED pattern being shown and carrying out [of Si single crystal substrate] incidence of the electron ray from [110].

[Drawing 6] It is the drawing substitution photograph in which the surface crystal structure of Si substrate of the example 5 which has the surface structure of 1x1 formed of Sr metal, Zr metal, and oxygen is shown, and is a diffraction pattern at the time of a RHEED pattern being shown and carrying out [of Si single crystal substrate] incidence of the electron ray from [110].

[Drawing 7] It is the drawing substitution photograph in which the surface crystal structure of Si substrate front face of 2x1 structure of the example of comparison where this invention is not processed is shown, and is a diffraction pattern at the time of a RHEED pattern being shown and carrying out [of Si single crystal substrate] incidence of the electron ray from [110].

[Drawing 8] Si -- formation -- 200 -- degree C -- having carried out -- a case -- others -- comparison -- an example -- depending -- Si -- a substrate -- a front face -- a front face -- the crystal structure -- being shown -- a drawing -- substitution -- a photograph -- it is -- a front face -- having been confused -- Si -- a front face -- RHEED -- an image -- being shown -- Si -- a single crystal -- a substrate -- [-- 110 --] -- a direction -- from -- an electron ray -- incidence -- having carried out -- an

[Drawing 9] It is a RHEED pattern on the front face of a film which grew epitaxially YSZ which is a dielectric thin film using Si substrate of this invention, and is a diffraction pattern at the time of carrying out [of Si single crystal substrate] incidence of the electron ray from [110].

[Translation done.]

* NOTICES *

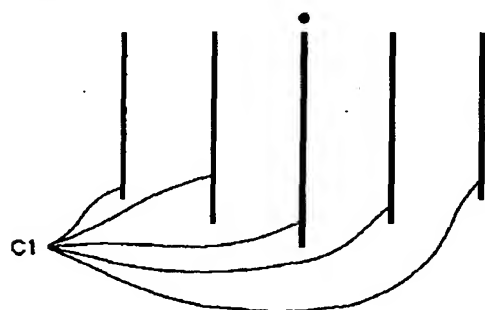
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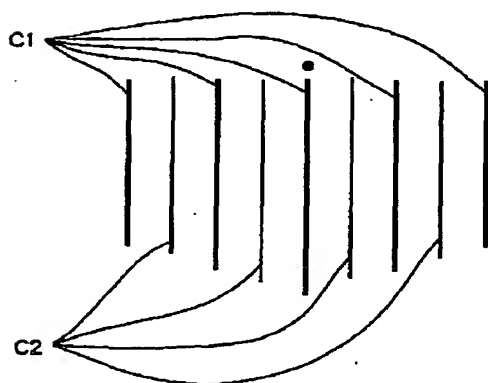
DRAWINGS

[Drawing 1]

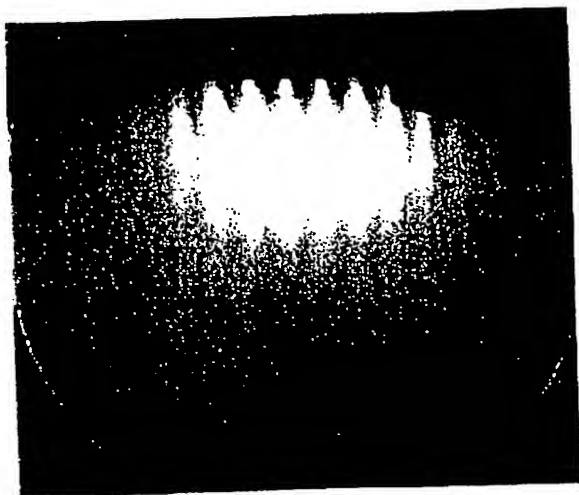
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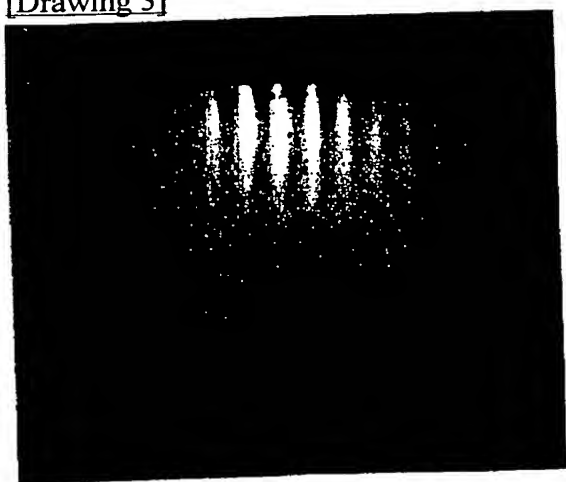
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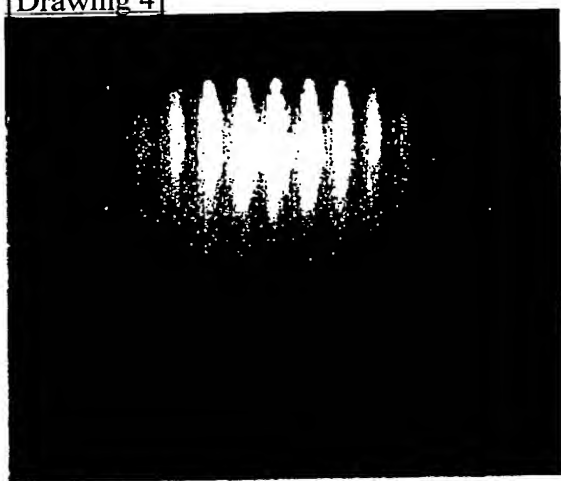
[Drawing 2]



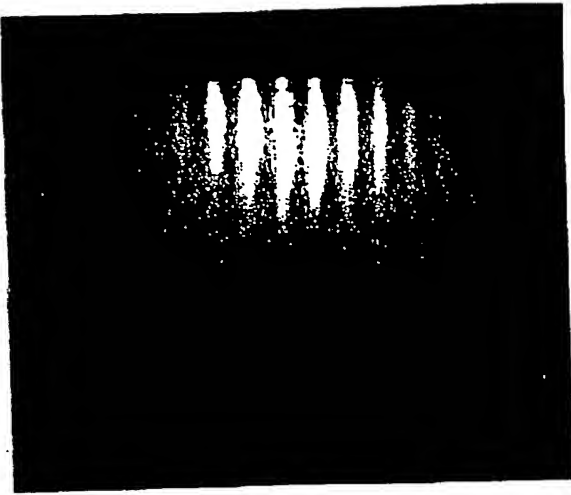
[Drawing 3]



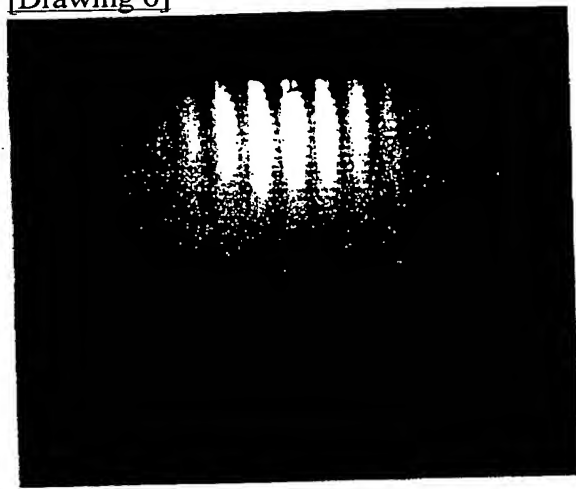
[Drawing 4]



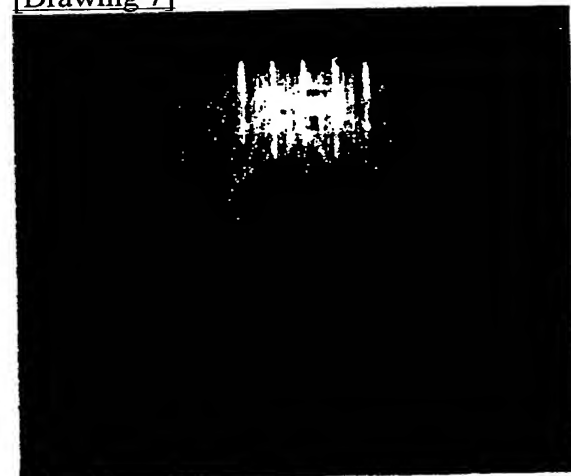
[Drawing 5]



[Drawing 6]



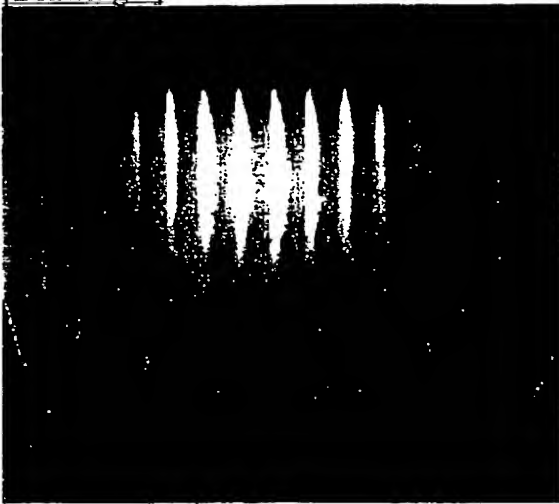
[Drawing 7]



[Drawing 8]



[Drawing 9]



[Translation done.]